

# **Calibration Gases for SCR and SNCR Process and Environmental Instrumentation**

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## **Summary**

With the enactment of the Clean Air Act Amendments in 1990 we have seen the market for NO<sub>x</sub> control grow exponentially; from virtually non-existent in 1990 to a forecasted billion plus dollars in 2002. During the same time period the allowable emission levels mandated by Federal and/or State regulations for NO<sub>x</sub> have decreased significantly. Today, it is not uncommon to see permits that require NO<sub>x</sub> levels in the single digit ppm range and, in fact, permits are being issued that require NO<sub>x</sub> emission levels of under 3 ppm.

In order to achieve these low levels of NO<sub>x</sub> emissions, power plants have had to install various types of post combustion deNO<sub>x</sub> processes. These processes are typically either SCR (Selective Catalytic Reduction) or SNCR (Selective Non-Catalytic Reduction). The primary difference between SCR and SNCR is the utilization of a catalyst in SCR. In both processes ammonia (NH<sub>3</sub>), in some form, is injected into the flue gas stream where it reacts with the NO<sub>x</sub> to form nitrogen (N<sub>2</sub>), and water (H<sub>2</sub>O). In order to properly control the deNO<sub>x</sub> process it is essential to know:

1. the NO<sub>x</sub> concentration leaving the combustion zone and prior to the deNO<sub>x</sub> reaction chamber
2. the NO<sub>x</sub> concentration post deNO<sub>x</sub>
3. the NH<sub>3</sub> concentration post deNO<sub>x</sub>

The knowledge of the NO<sub>x</sub> level prior to the deNO<sub>x</sub> is required to provide a feed forward signal for the control of the NH<sub>3</sub> feed rate. The NO<sub>x</sub> concentration post deNO<sub>x</sub> is required to provide a feed backward signal for the control of the NH<sub>3</sub> feed rate, as well as, for the reporting of emissions to the appropriate Federal and/or State agency. The measurement of the NH<sub>3</sub> concentration also provides both process information and regulatory data.

From a process standpoint the excess NH<sub>3</sub>, or slip, is an important parameter. NH<sub>3</sub> is expensive and the power plant wants to minimize the amount of slip to minimize operating costs. At the same time by tracking the percent NO<sub>x</sub> reduction versus slip over time the plant can monitor the efficiency of the deNO<sub>x</sub> process. From an environmental basis, permits have been issued limiting the levels of NH<sub>3</sub> emissions.

It should be noted that while accurate emission values are always necessary from a regulatory standpoint, in this era of NO<sub>x</sub> allowance markets accurate defensible values become extremely important from an operational standpoint. To this end the design, procurement, installation and operation of high quality CEMS (Continuous Emissions Monitoring Systems) becomes a necessity rather than a luxury.

Part of the on-going maintenance of a CEMS requires the regular, typically daily, calibration of the entire system. This is accomplished by the injection of a calibration gas. This injection is normally performed automatically by

the CEMS and does not require any personnel involvement. There are basically two levels of gases that are used by CEMS, certified standards and US EPA Protocol standards. Occasionally, for marketing purposes, gas vendors may define other levels.

A certified standard is a specialty gas calibration mixture with a known pedigree specifying 1) certified gas concentration, 2) traceability, 3) blend tolerance, 4) analytical certification accuracy and 5) certification period (shelf life). It is important when using certified standards that the pedigree be fully documented to insure meeting all legal requirements.

A US EPA Protocol standard is a calibration mixture that is produced in complete accordance with “EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, EPA-600/R-97/121” or the most current version.

In order to produce a US EPA Protocol Standard, NIST (National Institute of Science and Technology) or their internationally accepted counterparts have to produce and provide a standard reference material (SRM) for use by the gas manufacturers during analysis of the final product.

Currently the following gases are available as US EPA Protocols: carbon dioxide (CO<sub>2</sub>) in air or nitrogen, carbon monoxide (CO) in air or nitrogen, hydrogen sulfide (H<sub>2</sub>S) in nitrogen, methane (CH<sub>4</sub>) in air or nitrogen, nitric oxide (NO) in nitrogen, nitrous oxide (NO<sub>2</sub>) in air, oxygen (O<sub>2</sub>) in nitrogen, propane (C<sub>3</sub>H<sub>8</sub>) in air or nitrogen, and sulfur dioxide (SO<sub>2</sub>) in air or nitrogen. NH<sub>3</sub> is not available as a protocol since standards are not available from NIST or their counterparts.

In the past many manufacturers produced certified and US EPA Protocol calibration gas standards. Today, however, only a small percentage of the manufacturers are capable of producing the low NO<sub>x</sub> protocols and/or the NH<sub>3</sub> calibration standards now required for the operation and environmental monitoring/reporting of SCR and SNCR emissions. The issues involved in producing low level standards include such items as cylinder preparation, cylinder passivation, purity of raw materials, purity of balance gas, availability of analytical equipment, availability of analytical standards, availability of highly skilled production and analytical people and last but not least that the manufacturer has in place a rigorous quality control program.

Quality control, which is crucial when producing any product, is an essential element in producing the gaseous standards necessary for the SCR/SNCR marketplace. Since both regulatory compliance and allowance trading rely upon the values reported by the CEMS, and the CEMS values are only as good as the calibration standards, it is of utmost importance that the calibration standards be of the highest quality. Certification to ISO 9000 is an accepted method of insuring that a gas manufacturer has proper quality procedures in effect.

High quality calibration gases are normally produced gravimetrically, i.e. by weight. In a typical gas cylinder that contains 4000 liters of product, 0.5 ppm NO in a balance of N<sub>2</sub> would require just 0.00268 grams of NO and 5000 grams of N<sub>2</sub>. It is thus apparent that in order to produce a quality product the manufacturer has to have, in addition to all the items that were previously stated, the equipment necessary to accurately weigh the required small quantities.

While this presentation confines itself to low level NO and NH<sub>3</sub> calibration gases, it should be noted that new regulatory requirements for low level carbon monoxide (CO), mercury (Hg), and volatile organic compounds (VOCs) impose the same if not greater difficulties in the manufacturing process. It is therefore vital that the plant personnel responsible for calibration gas purchases understand what is required to insure that the plant operates efficiently and stays in compliance with all regulatory requirements.